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DETERMINATION OF FLUOROCARBON ETHER AUTOXIDATIVE DEGRADATION ME--ETC(U)

AUG 77 K L PACIOREK, R H KRATZER, J KAUFMAN

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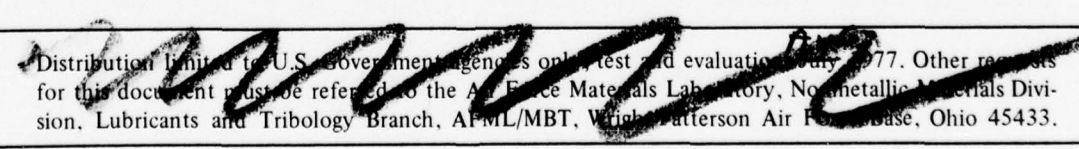
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Final Report for Period 16 June 1975 through 15 June 1977


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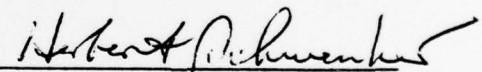
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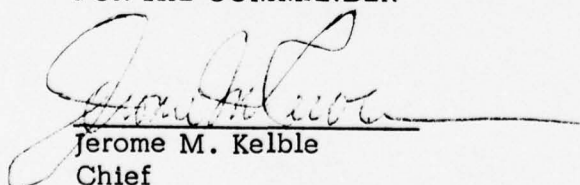


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Elucidation of mechanisms operative in thermal oxidative degradation of hexafluoropropene oxide derived polyethers and the effect of metals and anti-oxidant/anti-corrosion additives on this process are reported. Thermal oxidative instability of the commercial fluid, Krytox MLO-71-6, at moderate temperatures (550°F) was found to be due to the presence of ~3% of hydrogen terminated chains; treatment at 650°F in oxygen volatilized these chains

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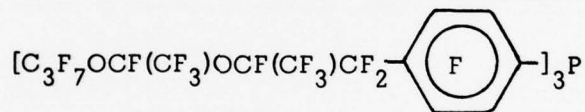
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by unzipping. The hydrogen-free fluid was unaffected by oxygen at 650°F and by M-50 and Ti(4Al, 4Mn) alloys at 600°F in oxidizing atmospheres. M-50 alloy catalyzed the degradation of the hydrogen terminated chains below and at 600°F, but did not affect the remainder of the fluid at these temperatures. At 650°F a chain scission process promoted by the metals constituting the alloy or their oxides or fluorides came into play. Ti(4Al, 4Mn) alloy in the presence of CF₃COF and COF₂, formed via decomposition of hydrogen terminated chains, degraded poly(hexafluoropropene oxide) fluids at 550°F by chain scission.

The additive MLO-76-30 arrested Krytox MLO-71-6 thermal oxidative degradation at 600°F and below both in the absence and in the presence of metals by preventing the degradation of the hydrogen terminated chains. Based on oxygen consumption and volatiles production, the additive's effectiveness at 600°F was time limited and at 650°F it was completely inactive both in the presence and absence of M-50. ↑

The structure of MLO-76-30 is as follows:



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FOREWORD

This report was prepared by Ultrasystems, Inc., Irvine, California under Contract No. F33615-75-C-5201, "Determination of Fluorocarbon Ether Autoxidative Degradation Mechanism," and covers work performed during the period 16 June 1975 through 15 June 1977. The Contract was initiated under Project No. 2303, "Fundamental Basic Research on Material Leading to Superior Non-metallic Materials Required in Advanced Air Force Systems," Task No. 2303Q3, "Polymer Research on Structural Materials and Environment Resistant Materials." The investigations were carried out by R. H. Kratzer, J. Kaufman, J. H. Nakahara and K. L. Paciorek, Project Manager. This contract was administered under the direction of the Air Force Materials Laboratory, Lubricants and Tribology Branch, Mr. C. E. Snyder (AFML/MBT), Project Engineer.

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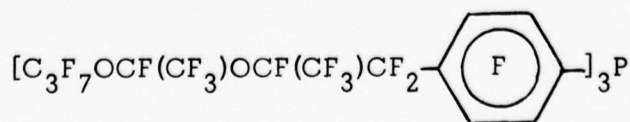
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SUMMARY

Elucidation of mechanisms operative in thermal oxidative degradation of hexafluoropropene oxide derived polyethers and the effect of metals and anti-oxidant/anti-corrosion additives on this process are reported. Thermal oxidative instability of the commercial fluid, Krytox MLO-71-6, at moderate temperatures (550°F) was found to be due to the presence of $\sim 3\%$ of hydrogen terminated chains; treatment at 650°F in oxygen volatilized these chains by unzipping. The hydrogen-free fluid was unaffected by oxygen at 650°F and by M-50 and Ti(4Al, 4Mn) alloys at 600°F in oxidizing atmospheres. M-50 alloy catalyzed the degradation of the hydrogen terminated chains below and at 600°F , but did not affect the remainder of the fluid at these temperatures. At 650°F a chain scission process promoted by the metals constituting the alloy or their oxides or fluorides came into play. Ti(4Al, 4Mn) alloy in the presence of CF_3COF and COF_2 , formed via decomposition of hydrogen terminated chains, degraded poly(hexafluoropropene oxide) fluids at 550°F by chain scission.

The additive MLO-76-30 arrested Krytox MLO-71-6 thermal oxidative degradation at 600°F and below both in the absence and in the presence of metals by preventing the degradation of the hydrogen terminated chains. Based on oxygen consumption and volatiles production, the additive's effectiveness at 600°F was time limited and at 650°F it was completely inactive both in the presence and absence of M-50.

The structure of MLO-76-30 is as follows:



SECTION I

INTRODUCTION

Polyperfluoroalkylethers, as represented by the Krytox family of fluids, possess remarkable thermal stability associated with low pour points and low vapor pressures. These properties render these compositions attractive candidates for high performance hydraulic fluids, oils, and greases. However, their oxidative stability is limited to approximately 550°F and above this temperature these materials are incompatible with ferrous and titanium alloys.

In the absence of information concerning the mechanisms of the reactions these fluids undergo with oxygen and metals, it is difficult if not impossible, to devise improvements which would prevent these undesirable processes from occurring. Additives were developed which are reported to extend the useful operation temperatures up to 650°F¹, but again their mode of action is largely unknown.

Thus, the objective of this contract was to elucidate the mechanisms involved in the oxidative degradation of polyperfluoroalkylether fluids at temperatures up to 650°F. Specifically, the aim was to establish the effects that ferrous alloys and titanium alloys have on the degradation mode of the fluids under investigation and to determine to what extent metal surfaces are affected when in contact with polyperfluoroalkylether fluids at elevated temperatures. A further objective was to study the action of selected anti-oxidant/anti-corrosion additives on the fluid degradation process.

SECTION II

RESULTS AND DISCUSSION

The investigations performed on the commercial grade hexafluoropropene oxide derived fluids of the general formula $C_3F_7[OCF(CF_3)CF_2]_x-OCF(CF_3)X$ (X presumed to be F) showed these compositions to be unstable in air above $550^{\circ}C$ in the presence of metals. This degradative action could be arrested to a degree by addition of phosphines and related compounds¹⁻⁵. It has been claimed that the fluorine end-capped materials have an incipient decomposition temperature slightly above $410^{\circ}C$ ($770^{\circ}F$) and that the presence of oxygen does not accelerate the degradation process^{6,7}. These data applied to well characterized materials wherein the end group denoted by X in the above formula was definitely a fluorine atom. Whether this was also true for the commercial grade products, namely the Krytox family of fluids, has not been verified. Furthermore, it is unknown whether the commercial fluids contain impurities which can trigger or catalyze the onset of degradation. In view of this possible variation in composition the majority of the investigations performed under this program utilized a specific batch of Krytox 143 AC fluid, namely Krytox MLO-71-6, with limited work conducted on other batches to supplement and confirm conclusions reached.

To obtain meaningful results leading to elucidation of the operative mechanisms a number of parameters needed to be established:

- a) Thermal stability of Krytox MLO-71-6 both alone and in the presence of metal or metals
- b) Thermal oxidative stability of Krytox MLO-71-6 both alone and in the presence of metal or metals
- c) Effect of additives on the above processes

In this program oxygen consumption and volatiles production were the primary and quantitative criteria of the degradation extent. The changes in viscosity, and molecular weight of the residual fluid together with the metal corrosion characteristics, i.e. appearance, weight loss or gain, and limited surface studies provided additional but mainly qualitative data.

The studies performed on Krytox fluids in the absence of metals are summarized in Table 1, whereas the volatiles produced in these tests are listed in Table 2. Parallel data obtained for experiments utilizing M-50 coupons are compiled in Tables 3 and 4 with additional analytical results pertaining to the products evolved being given in Table 5.

1. Mechanistic Considerations of Volatiles Production

Gumprecht, et al.^{6,7} have shown that the thermal decomposition of poly(hexafluoropropene oxide), $C_3F_7OCF(CF_3)CF_2[OCF(CF_3)CF_2]_x-OCF(CF_3)F$ produces in vacuo as the main products $CF_3CF=CF_2$, CF_3COF and COF_2 . Examining Tables 2 and 4, it is apparent that the major products formed in the investigations reported here were SiF_4 and CO_2 together with some BF_3 . No hexafluoropropene was detected under oxidizing conditions, although it was one of the main products observed in the tests conducted in nitrogen atmospheres as shown by Run 11 (see Tables 1 and 2). This instability of fluorinated olefins in the presence of oxygen has been established by studies conducted on Teflon where in oxygen no tetrafluoroethylene was observed.⁸ The following process could be responsible for hexafluoropropene consumption,

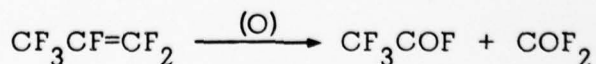


TABLE I
EXPERIMENTAL DATA FOR THERMAL DEGRADATION STUDIES
OF KRYTOX FLUIDS ^a

Test No. ^b	Starting Material Used g	Atm	Temp °F	Duration hr	Viscosity ^c Change %	MW ^d	Oxygen Consumed			Total Products		Krytox Consmd. mg	O/C ₃ F ₆ O Ratio atm/mol
							Total mg	% ^e	mg/g ^f	mg	mg/g ^g		
1	10.43	Air	610	24	-0.38	5500	1.7	32	0.16	13.7	1.3	-	-
2	11.82	Air	540	24	-	5500	1.2	22	0.10	12.3	1.0	-	-
3	11.33	N ₂	610	24	-	5500	-	-	-	0.7	0.1	-	-
4	11.87	N ₂	610	216	-	5500	-	-	-	11.5	1.0	-	-
5	12.05	Air	610	216	+0.80	5500	11.9	100	0.98	130.6	10.8	-	-
6	18.59	Air	650	24	+0.89	5500	11.6	100	0.62	159.3	8.6	-	-
7	20.76	Air	650	24	+0.60	5500	51.0	84	2.46	338.3	16.3	-	-
8	3.55	Air	650	24	+3.70	5600	17.0	27	4.79	152.3	42.9	-	-
9	3.42	O ₂	650	24	+5.47	5600	17.9	6.1	5.24	181.4	53.1	-	-
10	3.28	O ₂	650	216	+6.01	5600	24.8	8.4	7.56	238.0	72.6	-	-
11	10.26	N ₂	650	216	+1.02	5500	-	-	-	64.7 ^h	6.3	-	-
15	28.96	O ₂	650	208	+2.39	-	n.d.	-	-	2141	73.9	-	-
19	16.74	O ₂	650	24	+1.62	5500	90.0	31.3	5.38	805.7	48.1	560	1.67
22	12.44	O ₂	650	120	+2.63	5500	88.9	30.8	7.15	780	62.6	410	2.25
23 ^a	13.49	O ₂	650	24	+1.88	5000	77.5	26.8	5.74	731.1	54.2	480	1.68
25 ⁱ	13.23	O ₂	650	24	+0.73 ^j	5400 ^k	80.8	27.6	6.11	802.1	60.6	550	1.52
27 ^l	12.55	O ₂	650	24	+1.27	5400	39.1	12.6	3.12	308.3	24.6	230	1.76
34A	13.43	O ₂	600	24	-	-	21.4	7.5	1.59	252.6	18.8	-	-
34B	13.26	O ₂	600	192	+2.51	5200	40.8	14.4	3.08	381.1	28.7	-	-
41 ^l	12.47	O ₂	600	24	+1.39 ^j	-	2.2	0.8	0.18	2.2	0.2	-	-

a) In Test No. 23 Krytox MLO-76-28 was used, in all other tests Krytox MLO-71-6 was employed. b) Test Nos. 1-5 were performed in 50 ml sealed ampoules totally enclosed in the furnace; Test No. 6 was conducted in a 90 ml sealed ampoule; the remainder of the tests were performed in 438 ml apparatus in which only the liquid portion of the sample was at the denoted temperature. c) All the measurements were conducted at 100 ± 0.02 °F using Cannon-Manning semi-microviscometers; if differences between untreated Krytox fluids and a given sample were less than 0.35%, these are not listed. d) The molecular weight of untreated Krytox MLO-71-6 was found to be 5500; that of Krytox MLO-76-28 was found to be 4800. e) Percent of the oxygen available. f) Oxygen consumed in mg/g of Krytox employed. g) Products formed in mg/g of Krytox employed. h) This includes 0.7 mg in the -78°C fraction which could not be quantitatively determined due to small sample size. i) This test was performed using 1% of MLO-76-30 in MLO-71-6. j) The viscosity of the solution of 1% of MLO-76-30 in MLO-71-6 prior to heat treatment was + 0.85 with respect to Krytox MLO-71-6. k) The molecular weight of 1% of MLO-76-30 in MLO-71-6 prior to heat treatment was 5400. l) This test was performed using a silvered reaction tube.

TABLE 2
VOLATILE PRODUCTS OBTAINED ON THERMAL DEGRADATION OF KRYTOX FLUIDS^a

Test	CO		SiF ₄		CO ₂		BF ₃		COF ₂		CF ₃ COF		C ₃ F ₆		Others ^c	
	mg	% ^b	mg	% ^b	mg	% ^b	mg	% ^b	mg	% ^b	mg	% ^b	mg	% ^b	mg	% ^b
1	0.5	3.7	6.95	50.8	5.88	43.0	-	-	0.03	0.2	0.32	2.3	-	-	-	-
2	0.3	2.2	4.65	37.7	4.63	37.6	-	-	0.18	1.5	2.56	20.8	-	-	0.01	0.08
3	0.1	11.8	0.01	1.5	0.18	26.5	-	-	-	-	-	-	0.41	60.3	-	-
4	1.1	9.4	3.49	30.2	3.61	31.3	-	-	?	?	0.21	1.8	2.67	23.1	0.47	4.07
5	10.5	8.0	48.4	37.1	56.1	43.0	13.6	10.4	-	-	-	-	1.5	1.1	0.47	0.36
6	14.3	9.0	64.9	40.7	55.4	34.8	12.3	7.7	?	?	6.19	3.9	4.8	3.0	0.25	0.16
7	19.3	5.7	127.1	37.6	113.2	33.5	14.1	4.2	3.27	1.0	57.2	16.9	-	-	-	-
8	9.4	6.2	77.1	50.6	48.8	32.0	14.8	9.7	1.38	0.9	0.81	0.5	-	-	-	-
9	3.8	2.1	83.3	45.9	77.7	42.8	15.9	8.8	0.27	0.1	0.65	0.4	-	-	-	-
10	0.6	0.2	122.7	51.6	97.1	40.8	17.6	7.4	-	-	-	-	-	-	-	-
11	4.8	7.4	22.7	33.5	15.6	24.1	0.33	0.5	?	?	1.05	1.6	18.1	28.0	2.4	3.7
19	1.0	0.1	366.1	45.4	226.3	28.1	72.5	9.0	26.9	3.3	117.7	13.9	-	-	1.2	0.1
22	1.2	0.2	415.3	53.3	293.8	37.7	65.3	8.4	-	-	3.3	0.4	-	-	-	-
23	3.4	0.5	312.2	42.7	257.6	35.2	71.6	9.8	8.0	1.1	79.2	10.8	-	-	-	-
25 ^d	11.2	1.4	352.2	43.9	291.8	36.4	87.1	10.9	4.5	0.6	55.3	6.9	-	-	-	-
27 ^e	5.2	1.7	175.8	59.1	114.4	38.5	-	-	0.4	0.1	1.5	0.5	-	-	-	-
34A	1.5	0.6	68.7	27.2	44.3	17.5	10.9	4.3	27.5	10.9	92.9	36.8	-	-	6.8	2.7
34B	3.6	0.9	221.7	58.2	127.9	33.6	26.6	7.0	0.3	0.1	1.0	0.3	-	-	-	-

a) In the test No. 23 Krytox MLO-76-28 was used; in all other tests Krytox MLO-71-6 was employed.
b) Weight percent of total products. c) These in certain instances were identified and quantitated and are given in Table 5. d) In this test 1% of MLO-76-30 in Krytox MLO-71-6 was employed; in addition to the species listed a trace of PF₃ was also detected. e) This test was performed using a silvered reaction tube.

TABLE 3
EXPERIMENTAL DATA FOR THERMAL DEGRADATION STUDIES OF
M-50 METAL IN KRYTOX FLUIDS ^{a, b}

Test No.	Fluid Used g	Atm	Temp °F	Duration hr	Viscosity Change %	MW ^d	Oxygen Consumed			Total Products		Krytox Consumd. mg	O/C ₃ F ₆ O Ratio atm/mol	Coupon Weight Gain/Loss mg/cm ² h
							Total mg	% ^e	mg/g ^f	mg	mg/g ^g			
12	12.22	O ₂	550	24	-	5500	9.0	3.1	0.74	48.5	4.0	-	-	+ 0.18
13	12.13	O ₂	600	24	-	5600	70.8	24.6	5.84	576.7	47.5	340	2.16	+ 0.42
14	12.33	O ₂	650	24	+ 1.52	5500	82.5	28.9	6.69	798.3	64.7	560	1.53	+ 0.42
16 ⁱ	12.01	O ₂	650	24	+ 1.90	5600	27.3	9.6	2.27	184.9	15.4	-	-	+ 5.0
17	12.96	O ₂	650	216	+14.93	6900	283.0	100	21.8	2623.5	202	1580	1.86	- 6.3
18	12.80	N ₂	650	216	-	6500	-	-	-	47.7	3.7	-	-	+ 0.6
20 ^j	12.87	O ₂	650	24	+ 1.49	5900	96.0	32.6	7.46	826.0	64.1	520	1.92	+ 0.87 ^k
21	12.90	O ₂	600	216	+ 2.98	5500	94.9	33.3	7.36	774.9	60.1	490	2.01	+ 3.0
24 ^a	12.81	O ₂	650	24	+ 1.26	5000	108.5	37.1	8.47	1021.0	79.7	690	1.63	+ 0.67
26 ^l	14.28	O ₂	650	24	- 0.47 ^m	5400 ⁿ	91.9	31.8	6.44	830.8	58.2	610	1.56	+ 0.67
28A ^o	12.93	O ₂	650	48	n.d.	-	118.6	42.1	9.17	1050.4	81.2	-	-	n.d.
28B	12.19	O ₂	650	48	n.d.	-	130.3	45.2	10.7	1143.5	93.8	-	-	n.d.
28C	11.39	O ₂	650	48	n.d.	-	242.9	83.5	21.3	2180.0	191	-	-	n.d.
28D	9.86	O ₂	650	24	n.d.	-	117.0	40.4	11.9	997.2	101	-	-	n.d.
28E	9.16	O ₂	650	24	- 8.13	5000	97.8	34.0	10.7	891.8	97.4	-	-	-22.7
29 ^l	13.28	O ₂	600	24	+ 0.76 ^m	5400 ⁿ	1.2	0.4	0.09	3.3	0.2	-	-	+ 0.36
30 ^l	5.46	O ₂	600	233	- 0.38 ^m	5500 ⁿ	90.4	31.5	14.0	900.1	139	650	1.54	-24.4
31A ^p	12.28	O ₂	600	48	n.d.	-	2.5	0.9	0.20	8.7	0.7	-	-	n.d.
31B	12.27	O ₂	600	24	n.d.	-	1.8	0.6	0.15	7.8	0.6	-	-	n.d.
31C	12.27	O ₂	600	24	n.d.	-	6.5	2.3	0.53	11.9	1.0	-	-	n.d.
31D	12.26	O ₂	600	24	n.d.	-	8.9	3.1	0.72	15.7	1.3	-	-	n.d.
31E	12.25	O ₂	600	24	n.d.	-	7.8	2.7	0.64	15.0	1.2	-	-	n.d.
31F	12.24	O ₂	600	24	n.d.	-	9.5	3.3	0.78	32.1	2.6	-	-	n.d.
31G	12.22	O ₂	600	24	n.d.	-	22.1	7.7	1.81	238.2	19.5	-	-	n.d.
31H	12.06	O ₂	600	24	- ^m	5600	25.1	8.7	2.08	278.5	23.1	-	-	-32.7
33 ^j	13.21	O ₂	650	48	+ 0.64	n.d.	120.7	41.7	9.14	1276.8	96.7	770	1.63	+ 1.28 ^k
35 ⁱ	9.37	O ₂	600	24	+ 3.20	5600	~2.0	0.7	0.21	2.2	0.2	-	-	+ 0.30

a) In Test No. 24 Krytox MLO-76-28 was used, in all the other tests Krytox MLO-71-6 was employed. b) In these tests only the liquid portion of the sample was at the denoted temperature; the apparatus used was equipped with a finger-like projection, the volume of the apparatus minus the Krytox (ca 12 g) was 416 ml. c) All the measurements were conducted at 100 ± 0.02°F using Cannon-Manning semi-microviscometers. If differences between untreated Krytox fluids and a given sample were less than 0.35%, these were not listed. d) The molecular weight of the untreated Krytox MLO-71-6 was found to be 5500; that of Krytox MLO-76-28 was found to be 4800. e) Percent of the oxygen available. f) Oxygen consumed in mg/g of Krytox employed. g) Products formed in mg/g of Krytox employed. h) The area of the coupon (both sides, including the area of the pins) is 1.6459 cm². i) The Krytox fluid, MLO-71-6 used in this test was pretreated at 650°F (see Test No. 15). j) In this test three M-50 coupons were employed. k) This is the average weight gain of the three coupons. l) This test was performed using 1% of MLO-76-30 in MLO-71-6. m) The viscosity of the solution of 1% of MLO-76-30 in MLO-71-6 prior to heat treatment was +0.85 with respect to Krytox MLO-71-6. n) The molecular weight of 1% of MLO-76-30 in MLO-71-6 prior to heat treatment was 5400. o) Tests 28A-28D were performed stepwise, removing the condensibles and replenishing oxygen at times specified. The weight of fluid employed in Tests 28B-28E was calculated using the expression: 0.701 x weight of products formed = fluid weight loss. p) Tests 31A-H were performed using 1% of MLO-76-30 in MLO-71-6, removing the condensibles and replenishing oxygen at times specified. The weight of fluid employed in Tests 31B-31H was calculated using the expression: 0.734 x weight of products formed = fluid weight loss.

TABLE 4

VOLATILE PRODUCTS OBTAINED ON THERMAL DEGRADATION OF
KRYTOX FLUIDS IN THE PRESENCE OF M-50 METAL^a

Test	CO		SiF ₄		CO ₂		BF ₃		COF ₂		CF ₃ COF		C ₂ F ₆		CF ₄		C ₃ F ₆		Others	
	mg	% ^b	mg	% ^b	mg	% ^b	mg	% ^b	mg	% ^b	mg	% ^b	mg	% ^b	mg	% ^b	mg	% ^b	mg	% ^b
12	1.19	2.4	13.6	28.0	16.0	33.0	-	-	2.9	5.9	14.9	30.7	-	-	-	-	-	-	-	-
13	1.31	0.2	242.5	42.1	199.6	34.6	34.3	6.0	20.7	3.6	75.9	13.2	-	-	-	-	-	-	3.0	0.4
14	5.12	0.6	370.0	46.3	284.1	35.6	84.6	10.6	5.7	0.7	46.8	5.9	-	-	-	-	-	-	2.0	0.2
16	3.26	1.8	100.2	54.2	50.7	27.4	18.0	9.7	2.5	1.4	1.3	0.7	8.8	4.8	0.1	0.05	-	-	-	-
17	25.8	1.0	1464.4	55.8	853.6	32.5	158.6	6.0	-	-	-	-	115.8	4.4	0.3	0.01	-	-	4.0	0.2
18	3.85	8.1	14.7	30.8	10.6	22.2	1.1	2.3	-	-	?	?	-	-	-	-	15.0	31.4	2.4	5.0
20	4.53	0.5	477.2	57.8	237.3	28.7	63.9	7.7	5.8	0.7	27.6	3.3	9.5	1.2	-	-	-	-	0.3	0.04
21	4.15	0.5	423.7	54.6	283.0	36.5	57.7	7.4	2.2	0.3	-	-	4.1	0.5	0.1	0.01	-	-	-	-
24	4.9	0.5	588.0	57.6	331.8	32.5	69.8	6.8	5.6	0.5	20.9	2.0	-	-	-	-	-	-	-	-
26 ^c	10.6	1.3	261.4	31.4	309.9	37.3	109.8	13.2	16.0	1.9	123.1	14.8	-	-	-	-	-	-	-	-
28A	4.6	0.4	550.9	52.4	377.8	36.0	91.9	8.7	1.9	0.2	7.9	0.8	14.9	1.4	0.5	0.05	-	-	-	-
28B	4.1	0.4	474.8	41.5	463.0	40.5	129.2	11.3	4.8	0.4	12.4	1.1	53.9	4.7	1.5	0.13	-	-	-	-
28C	16.5	0.8	1011.2	46.4	766.8	35.2	247.9	11.4	9.3	0.4	5.2	0.2	119.3	5.5	3.8	0.17	-	-	-	-
28D	9.2	0.9	387.9	38.9	415.6	41.7	129.6	13.0	3.2	0.3	8.3	0.8	39.0	3.9	4.5	0.45	-	-	-	-
28E	11.0	1.2	426.6	47.8	287.9	32.3	117.9	13.2	1.6	0.2	5.1	0.6	36.5	4.1	5.2	0.58	-	-	0.1	3.0
29 ^c	-	-	1.5	45.5	1.7	51.5	-	-	-	-	-	-	-	-	-	-	-	-	-	-
30 ^c	38.0	4.2	458.5	50.9	272.0	30.2	95.2	10.6	3.0	0.3	7.9	0.9	21.4	2.4	4.1	0.46	-	-	-	-
31A ^c	1.2	13.8	2.6	29.9	2.5	28.7	-	-	-	-	-	-	-	-	-	-	-	-	2.4	27.6
31B ^c	1.0	12.8	1.5	19.2	2.1	26.9	-	-	-	-	-	-	-	-	-	-	-	-	3.2	41.0
31C ^c	1.4	11.8	0.4	3.4	4.1	34.5	-	-	-	-	-	-	-	-	-	-	-	-	6.0	50.4
31D ^c	1.8	11.5	0.8	5.1	6.7	42.7	-	-	-	-	-	-	-	-	-	-	-	-	6.4	40.8
31E ^c	2.2	14.7	2.8	18.7	6.7	44.7	-	-	-	-	-	-	-	-	-	-	-	-	3.3	22.0
31F ^c	4.0	12.5	11.0	34.3	12.6	39.3	-	-	0.4	1.2	1.3	4.0	-	-	0.1	0.31	-	-	2.7	8.4
31G ^c	12.2	5.1	106.0	44.5	65.2	27.4	18.8	7.9	10.0	4.2	16.6	7.0	Trace	-	0.1	0.04	-	-	9.3	3.9
31H ^c	15.7	5.6	124.0	44.5	91.7	32.9	21.7	7.8	5.7	2.0	13.5	4.8	1.7	0.6	0.1	0.05	-	-	4.4	1.6
33	7.5	0.6	742.5	58.2	346.3	27.1	135.8	10.6	4.6	0.4	10.9	0.9	23.1	1.8	6.1	0.48	-	-	-	-
35	?	?	?	?	2.1	95.5	?	?	?	?	?	?	?	?	?	?	?	?	0.1	4.5

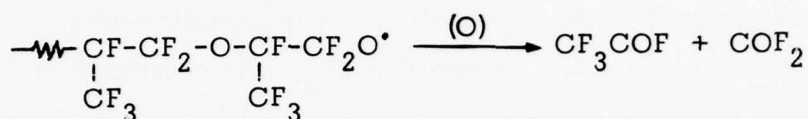
a) In Test No. 26 Krytox MLO-76-28 was used; in all the other tests Krytox MLO-71-6 was employed. b) Weight percent of total products. c) In this test 1% of MLO-76-30 in Krytox MLO-71-6 was employed.

TABLE 5
VOLATILES NOT IDENTIFIED IN PRECEDING TABLES

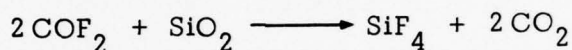
Test	C ₂ F ₄		C ₄ F ₈		C ₃ F ₆		C ₃ F ₇ H		C ₃ F ₆ H ₂		C ₄ F ₈ H ₂		C ₄ F ₉ H		C ₅ F ₁₁ H		C ₆ F ₁₃ H		C ₇ F ₁₅ H	
	mg	% ^a	mg	% ^a	mg	% ^a	mg	% ^a	mg	% ^a	mg	% ^a	mg	% ^a	mg	% ^a	mg	% ^a	mg	% ^a
1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4	0.01	0.08	0.07	0.61	0.08	0.69	0.03	0.26	-	-	-	-	0.12	1.05	0.16	1.40	-	-	-	-
5	-	-	-	-	0.31	0.24	0.01	0.01	-	-	0.06	0.05	0.02	0.02	-	-	-	-	-	-
6	-	-	0.04	0.02	0.12	0.08	T	-	-	-	-	-	0.05	0.03	-	-	-	-	-	-
7	-	-	-	-	T	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
11	0.25	0.43	0.28	0.48	0.23	0.39	0.09	0.15	-	-	-	-	0.46	0.79	0.19	0.32	0.47	0.80	0.23	0.39
18	0.28	0.59	0.26	0.55	0.30	0.63	0.14	0.29	-	-	-	-	0.76	1.59	0.08	0.17	0.44	0.92	0.10	0.21

a) Weight percent of total products.

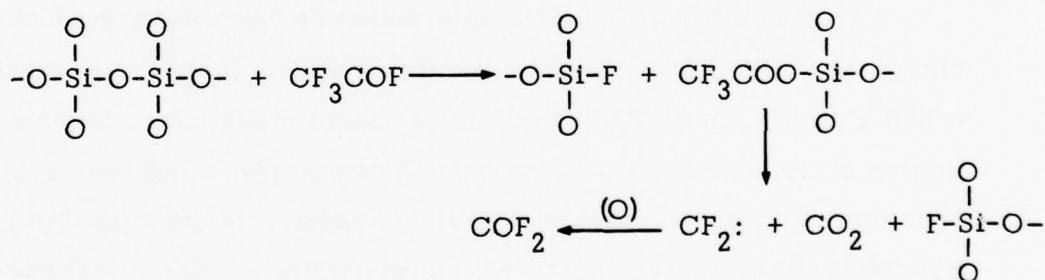
although it is more likely that in the presence of oxygen, the polymer radical unzips directly into CF_3COF and COF_2 , i.e.:



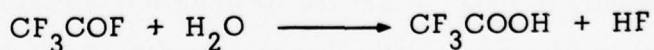
The production of CO_2 and SiF_4 is due to the reaction of the primary product such as COF_2 with the glass surface:



Regarding the fate of CF_3COF , several possibilities exist. Under the existing conditions, COF_2 might be predominantly formed or the originally liberated CF_3COF degrades further via salt type pyrolysis found to be operative in the case of e.g. the sodium salt of trifluoroacetic acid, i.e.:⁹



Another possible path involves hydrolysis followed by degradation, i.e.:



Since in all the tests only small quantities of CF_3H were found this process is either relatively unimportant or CF_3H once formed is

oxidized further. The production of volatile hydrogen-containing fluorocarbons is to be expected inasmuch as these types of products were also encountered in the degradation of perfluoroalkylether substituted heterocyclics^{10,11}. Regarding BF_3 , this compound is formed in a reaction analogous to that responsible for SiF_4 production.

Based on the above equations to degrade poly(hexafluoropropene-oxide) to CO_2 and SiF_4 requires two atoms or one molecule of oxygen per repeating unit of the polymer. Consequently the ratio of oxygen consumed per mole of hexafluoropropene oxide lost should be equal to 2. In the experiments where this ratio was measured (see Tables 1, 3 and 8) it varied from 1.5 to 2.2. If one considers the difficulty of weighing back accurately the remaining fluid the agreement with the theoretical value is not as bad as would appear from the observed spread.

To possibly eliminate the interaction of the primary products with glass walls one of the experiments (Test 27, Table 1) was conducted at 650°F in oxygen for 24 hr in a silver coated glass tube. At the conclusion of the heat treatment the portion of the tube which was submerged in the hot zone was covered by a yellow deposit. In the volatiles formed (see Table 2) no BF_3 was detected; consequently, it can be assumed that the yellow deposit was silver fluoroborate, AgBF_4 . Unfortunately, in view of the small quantity of the material produced, it could not be subjected to any analysis. Based on the oxygen consumed and volatiles formed, it appears that the degradation process is inhibited by the presence of silver salts. If one compares Tests 19 and 27 (see Table 2), the actual degradation in the silver coated tube is approximately 50% of that observed under normal conditions. The product mix is markedly different from that found in the absence of

silver; as noted, no boron trifluoride was detected and the quantities of CF_3COF and COF_2 were greatly reduced (indicating that these species reacted with silver). Also, the relative concentration of carbon monoxide was increased.

No further tests were performed in apparatus other than glass. In view of the reproducibility of the results obtained in glass tubes and the absence of volume to surface area effects upon degradation extent it seems reasonable to assume that glass affects only the degradation products not the process itself.

2. Degradation Studies in the Absence of Metal

Examining the data contained in Table 1, several points become apparent:

- a) In the absence of oxygen (air), even at 650°F , the extent of degradation as determined by volatiles produced is very low (see Test No. 11).
- b) In the presence of oxygen (air), the reaction at $540\text{--}610^\circ\text{F}$ is relatively limited, at least during the first 24 hr period, as indicated by the oxygen consumed and volatiles produced (Tests 2, 34A).
- c) At 650°F the final extent of degradation is more or less reached within the first 24 hr (compare Tests 9 and 10); no significant additional consumption of oxygen and volatiles production is observed during the following 192 hr.
- d) The rate or rather extent of reaction is not greatly affected by using pure oxygen instead of air (compare Tests 8 and 9) as long as the oxygen partial pressure is kept above a

certain minimum (compare Tests 1 and 34A), i.e. not more than 30% oxygen depletion in air is reached. (A consequence of this finding was that all further experiments were performed in pure oxygen which permitted the use of a relatively small apparatus.)

- e) The reaction rate is practically independent of the ratio of exposed liquid surface to liquid volume (compare Tests 9 and 19).
- f) Different batches of Krytox reached different extents of degradation under identical conditions (compare Tests 19 and 23).
- g) The fluid recovered after all the tests listed exhibited the same infrared spectral and DSC^{*} characteristics as the starting material. The changes in molecular weight and viscosity were experimentally not significant.
- h) The additive, MLO-76-30, was found to arrest the degradation at 600°F at least for the first 24 hr period (compare Tests 34A and 41); however, as determined by criteria employed under this program, it was completely ineffective at 650°F (compare Tests 19 and 25). This result is contrary to that reported by others¹.

Based on the findings cited above it can be deduced that up to 650°F Krytox is oxidatively stable. The limited degradation observed at 650°F must be due to an oxidative instability of some weak links or end groups present in the fluid. This oxidation of these end groups or at least the initial steps of this reaction must take place in the liquid phase and must, therefore, be caused by dissolved oxygen. The fact that neither the oxygen partial pressure in the gas phase (to a degree)

* DSC = differential scanning calorimetry

nor the liquid surface to volume ratio do significantly affect the extent of reaction in turn indicates that, at least over the time periods employed, the fluid must contain sufficient oxygen to produce "complete" reaction of these end groups and that, again within the time intervals studied, consumed dissolved oxygen must be replenished from the gas phase at a rate sufficient to maintain that oxygen concentration.

Inasmuch as the nature of the residual fluid was virtually the same as that of the starting material (molecular weight, viscosity, infrared spectral characteristics) and a specific constant degree of decomposition (as measured by oxygen consumed and volatiles formed) was reached reproducibly with a given fluid batch it must be deduced that a certain number of chains had to be hydrogen terminated. These would be oxidatively relatively unstable and once attacked would proceed to unzip. In this way only a limited number of volatiles would be formed, which was found to be the case (see Table 2) and once all the "weak" chains were consumed or "burned off" a stable fluid would result. It can be speculated that the additive arrests this process, at least at 600°F, most likely by reacting with the radicals originally formed. Based on the fluid consumed on prolonged exposure to oxygen at 650°F, the hydrogen terminated chains account for ca 3.3% of Krytox MLO-71-6. The theory that the weak links or rather end groups are indeed hydrogen atoms and that the additive action prevents the oxidation of these hydrogen terminated chains was subsequently supported by the finding that the additive MLO-76-30 effectively suppresses the degradation of $C_3F_7OCF(CF_3)CF_2[OCF(CF_3)CF_2]_xOCF(CF_3)H$ type fluids¹².

3. Degradation Studies in the Presence of M-50 Alloy

The degradation extent of Krytox MLO-71-6 in the presence of M-50 ball bearing alloy coupons in a non-oxidizing atmosphere, e.g. nitrogen, was found to be negligible even at 650°F (see Table 3, Test 18). It is apparent that degradation in oxygen at 550°F is also not very extensive (compare Tests 12 and 18), yet increases by a factor of ~10 when the temperature is raised to 600°F (see Test 13). The difference between the 600 and 650°F 24 hr treatments in oxygen (Tests 13 and 14) is surprisingly small and the values measured are fairly close to those found at 650°F in oxygen on prolonged heating in the absence of the alloy (compare with Tests 10 or 22, Table 1). Also surprising is the finding that the use of more than one M-50 coupon failed to affect the extent of degradation as compared to that reached using one coupon only (compare Tests 14 and 20, also 28A and 33). No really significantly increased degree of degradation was noted on heating the fluid in the presence of the M-50 coupon at 600°F in oxygen for 216 hr as compared to a 24 hr period (see Tests 13 and 21). This finding would then imply that at 600°F the metal is merely accelerating the rate of the oxidative degradation so that the extent reached at 600°F approaches or equates that found at 650°F under parallel conditions but in the absence of metal. It again supports the stipulations advanced above that this process must be due to some weak links, most likely hydrogen end groups.

The actual proof of the above theory is the stability of the fluid pretreated at 650°F in oxygen (see Test 15, Table 1) to M-50 coupon at 600°F in oxygen (see Test 35, Table 3) as shown by the minimal amounts of oxygen consumed and volatiles evolved in addition to the unchanged appearance of the metal coupon itself. Figure 1

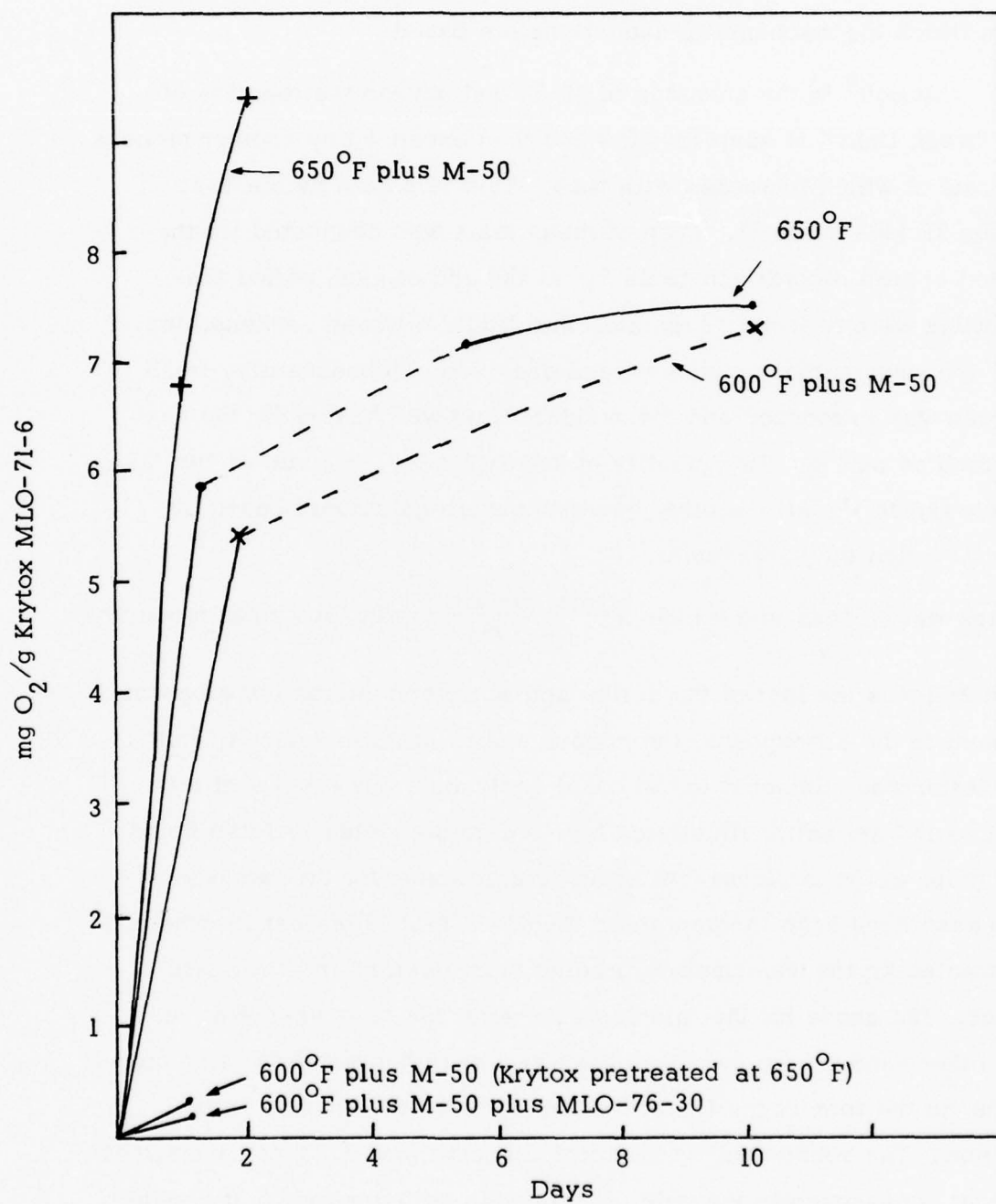


Figure 1. Oxygen Uptake by Krytox MLO-71-6 as Function of Time

is a graphical presentation of the results of these specific tests, upon which the mechanistic deductions are based.

At 650° in the presence of M-50 and oxygen the reaction of the "weak links" is supplemented and then exceeded by another process, the rate of which increases with time. This is shown by the Test Series 28 (see Table 3). Each of these tests was conducted for the period of time recorded in Table 3. At the end of each period the volatiles were removed, separated into liquid nitrogen condensibles and noncondensibles, measured and analyzed. Subsequently, fresh oxygen was introduced and the residual fluid was heated for the next designated period. The quantity of Krytox MLO-71-6 given in Test 28A was weighed in, all the other quantities were calculated based on Test 14 using the expression:

$$\text{Krytox weight loss in g} = 0.56 \times \frac{\text{total products}}{0.7983} = 0.701 \times \text{total products}.$$

Test 28E was the last of the series and at its conclusion the tube was opened to the atmosphere, the coupon and fluid were weighed, and the latter was subjected to the usual analyses. The results of this test series are better illustrated by the data presented in Table 6 and the graph given in Figure 2 wherein "corrections" for the "weak link process" have been incorporated; Test 14 - Test 19 or Test 16 (wherein pretreated Krytox was employed) being thus given as the first data point. The cause for the rate decrease after 168 hr is unknown, on the other hand it may be due to the metal or rather metal salts produced either in the form of the flaked-off "rust" or as the coating on the coupon. The coupon during the total exposure lost 9.3% of its original weight, consequently the bulk of metal was not consumed. It should be stressed that although viscosity was decreased by 8% (in all the

TABLE 6
SELECTED RATES OF OXYGEN CONSUMPTION AND
PRODUCT FORMATION AT 650°F IN OXYGEN ^a

Test No.	mg O ₂ /g	mg O ₂ /g/hr	mg Prod/g	mg Prod/g/hr
14	6.69	0.28	64.7	2.70
16 (pretreated fluid)	2.27	0.09	15.4	0.64
19 (no metal)	5.38	0.22	48.1	2.01
14-19	1.32	0.06	16.6	0.69
28A	9.17	0.19	81.2	1.69
28A-14	2.48	0.10	16.5	0.69
28B	10.69	0.23	93.8	1.95
28C	21.33	0.44	191	3.98
28D	11.87	0.49	101	4.21
28E	10.68	0.45	97.4	4.06

a) For experimental details see Tables 1 and 3.

TABLE 7
RATE OF OXYGEN UPTAKE AND PRODUCT EVOLUTION AS A FUNCTION
OF SUCCESSIVE EXPOSURES OF KRYTOX MLO-71-6 PLUS ADDITIVE
MLO-76-30 TO OXYGEN AT 600°F IN THE PRESENCE OF M-50

Test No.	mg O ₂ /g/24 hr	mg Prod/g/24 hr
29	0.09	0.25
31A-29	0.11	0.44
31B	0.15	0.64
31C	0.53	0.96
31D	0.72	1.28
31E	0.64	1.22
31F	0.78	2.62
31G	1.81	19.46
31H	2.08	23.09

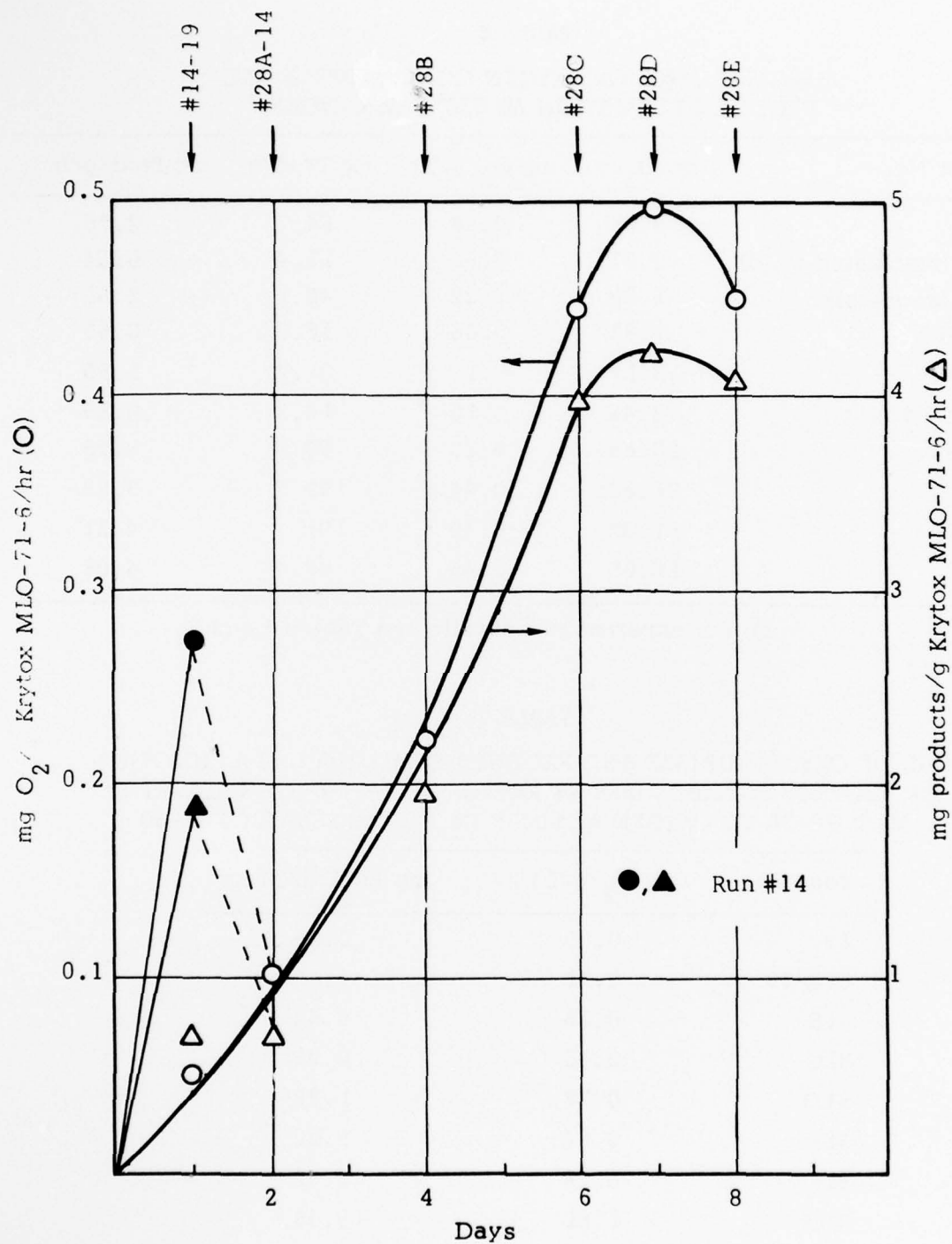


Figure 2. Rate of Oxygen Uptake and Product Evolution as a Function of Successive Exposures of Krytox MLO-71-6 to Oxygen at 650°F in the Presence of M-50 Coupon

other instances it was increased), no difference could be noted in the residual fluid neither by molecular weight measurement nor by infrared spectral analysis. One is, therefore, tempted to speculate that the rate increase observed with time of exposure is not caused by a change in the fluid but is due to production of active sites or species by the metal which promote scissions to occur, these being then followed by unzipping.

To assess the effect and efficiency of the anti-oxidant/anti-corrosion additive supplied by AFML, Runs 26, 29 and the Run 31 series were performed. As noted previously, the additive is not effective at 650°F (compare Tests 26 and 14, Table 3). This has nothing to do with the presence of metal since in the absence of M-50 essentially the same degradation behavior was observed (compare Test 25, Table 1). At 600°F, however, completely different results were obtained (see Run 29 and Test Series 31, Table 3) inasmuch as the degradation was greatly suppressed (compare Tests 13 and 29) as evidenced by oxygen consumed, products formed and coupon appearance and weight change. Over an extended period of time, the rate increase remained essentially the same (seven days), especially with respect to the volatiles formed. Yet, it can be seen that some oxidation of the additive itself was taking place after the third day. This is evident from the data presented in Tables 3 and 7 and especially from the graph given in Figure 3. Between the 7th and 8th day (see Run 31G), the rate of degradation increased markedly and from the break in the curve it can be deduced that a different mechanism comes into play at that stage. The latter assumption is supported by the nature of products formed and their relative distribution if one compares the results of Runs 13 and 31G (see Table 4). The action of the additive is still evident in Test 31G by the lower degradation rate, as compared to Test 13, and the higher relative

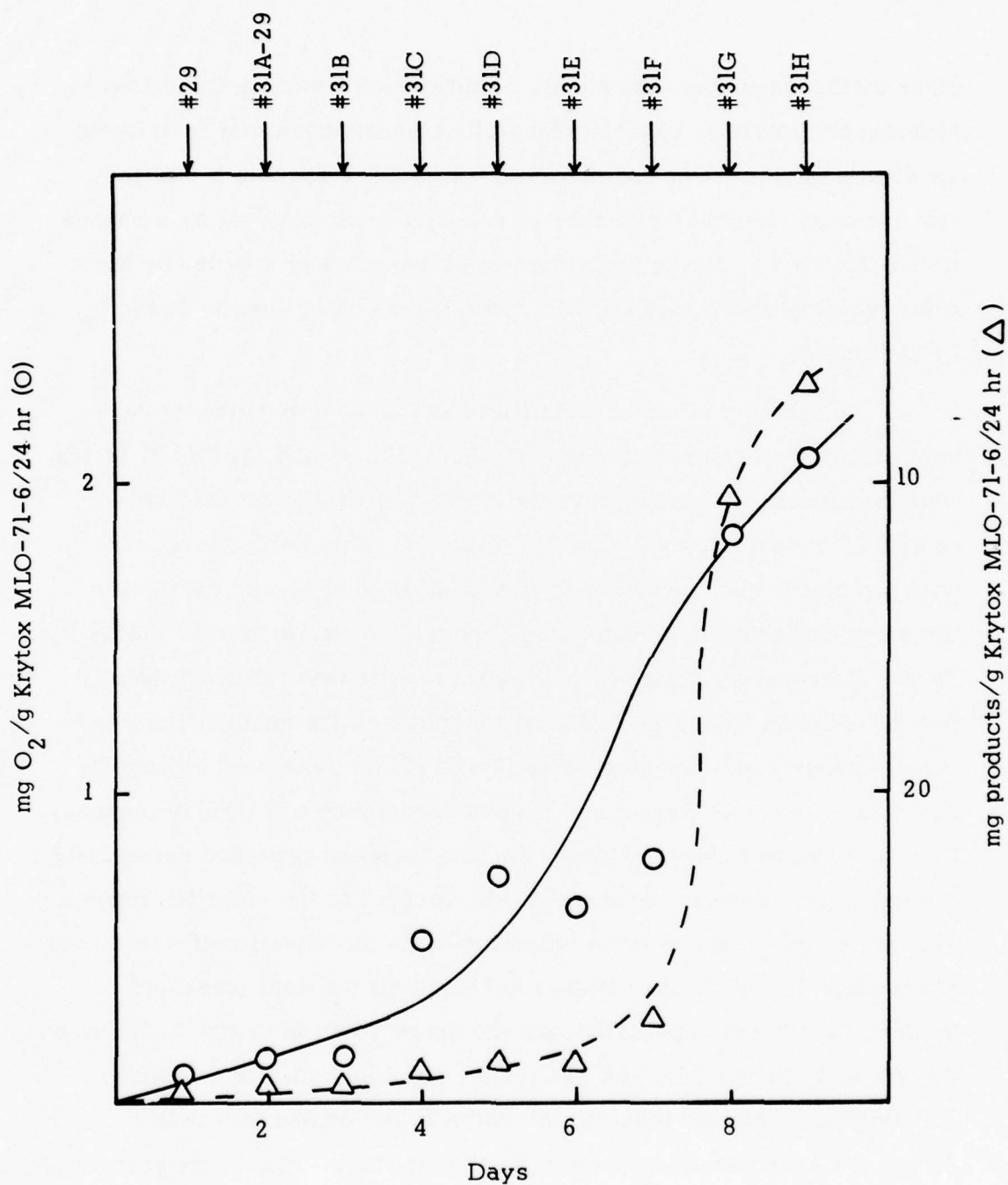


Figure 3. Rate of Oxygen Uptake and Product Evolution as a Function of Successive Exposures of Krytox MLO-71-6 Plus Additive MLO-76-30 to Oxygen at 600°F in the Presence of M-50 Coupon

proportion of carbon monoxide among the degradation products. Actually it should be noted that even after 9 days of heat treatment in oxygen the total oxygen consumed and products formed were somewhat lower than the values found under analogous conditions in the absence of the additive, i.e., 7.36 versus 6.91 and 6.01 versus 5.00 respectively (compare Test Series 31A through 31H with Test 21 and Test 13). Examining the data plotted in Figure 3 and adding the total oxygen consumed and volatiles formed, it is apparent that the additive is very effective for six days in limiting the extent of degradation. However, after the nine day period the degradation, especially with respect to coupon weight loss, becomes severe. It should be noted that the volatile product mix formed in the experiments utilizing the additive was significantly different from that found in the runs without additive, especially with respect to the CO quantities formed (see Table 4). Based on the studies performed it can be concluded that the additive acts by inhibiting the degradation of the fluid itself, not by interacting with the metal surface. The metal is unaffected because no corrosive, R_fCOF , type compounds are produced. Inasmuch as in the absence of the additive the metal does accelerate the degradation of the weak-ended chains it can be further speculated that this catalyzing action is due to metal fluorides. It is believed that given sufficient time in the presence of oxygen at $600^{\circ}F$ all the hydrogen terminated chains would be degraded even in the absence of metal, i.e. a degradation level identical to that found at $650^{\circ}F$ would be reached.

4. Degradation Studies in the Presence of Ti(4Al, 4Mn) Alloy

The investigations conducted utilizing Ti(4Al, 4Mn) alloy in Krytox MLO-71-6 fluid are summarized in Table 8 and the type and quantities of the volatiles liberated are given in Table 9. Comparing

TABLE 8
EXPERIMENTAL DATA FOR THERMAL DEGRADATION STUDIES
OF Ti(4Al, 4Mn) ALLOY IN KRYTOX FLUID a, b

Test No.	Fluid Used g	Atm	Temp °F	Period hr	Viscosity Change %	MW ^d	Oxygen Consumed			Total Products		Krytox Consmd. mg	O/C ₃ F ₆ O Ratio atm/mol	Coupon Weight Gain/Loss mg/cm ² 2h
							Total mg	% ^e	f mg/g	mg	mg/g			
36	11.40	O ₂	600	24	-21.6	4900	174.0	60.6	15.3	1617.9	142	1170	1.54	-0.17
37	11.02	O ₂	550	24	-	5400	18.8	6.5	1.71	183.2	16.6	100	1.95	+0.17
39A ⁱ	12.91	O ₂	550	48	n.d.	n.d.	66.3	23.1	5.14	622.6	48.2	n.d.	-	n.d.
39B	12.53	O ₂	550	48	n.d.	n.d.	182.7	63.5	14.6	1824.4	146	n.d.	-	n.d.
39C	11.15	O ₂	550	24	-44.8	4200	122.6	42.0	11.0	1236.9	111	n.d.	-	-0.68
40 ^j	13.24	O ₂	550	24	+1.18 ^k	n.d.	1.8	0.6	0.14	2.6	0.2	-	-	0
42 ^j	12.72	O ₂	600	24	+0.94 ^k	n.d.	2.6	0.9	0.20	1.6	0.1	-	-	0
43 ^l	12.23	O ₂	550	24	+1.73	5500	2.4	0.8	0.20	2.9	0.2	-	-	0
44 ^l	10.80	O ₂	605	24	+0.38	5500	5.5	1.9	0.51	48.4	4.5	-	-	+0.17
45	12.44	N ₂	605	24	+0.80	5500	-	-	-	1.4	0.1	30	-	+0.06
46 ^m	12.08	O ₂	600	24	-30.1	4700	221.8	75.7	18.4	2127.3	176	133	1.73	-0.07 ⁿ

a) The Krytox used was MLO-71-6. b) In those tests only the liquid portion of the sample was at the denoted temperature; the apparatus used was equipped with a finger-like projection, the volume of the apparatus minus the Krytox (ca 12 g) was 416 ml. c) All the measurements were conducted at 100 ± 0.02 °F using Cannon-Manning semi-microviscometers; if differences between untreated Krytox fluids and a given sample were less than 0.35%, these were not listed. d) The molecular weight of the untreated Krytox MLO-71-6 was found to be 5500. e) Percent of the oxygen available. f) Oxygen consumed in mg/g of Krytox employed. g) Products formed in mg/g of Krytox employed. h) The area of the coupon (both sides, including the area of the rims) is 1.7735 cm². i) Tests 39A-39C were performed by removing the condensibles and replenishing oxygen at times specified. The weight of fluid employed in Tests 39B and 39C was calculated using the expression: 0.723 x weight products formed = fluid weight loss. j) This test was performed using 1% of MLO-76-30 in MLO-71-6. k) The viscosity of the solution of 1% of MLO-76-30 in MLO-71-6 prior to heat treatment was +0.85 with respect to Krytox MLO-71-6. l) These tests were performed using Krytox MLO-71-6 which was pretreated in oxygen at 650 °F for 168 hr. m) In this test three Ti(4Al, 4Mn) coupons were employed. n) This is the average weight change of the three coupons.

TABLE 9

VOLATILE PRODUCTS OBTAINED ON THERMAL DEGRADATION OF
KRYTOX FLUID MLO-71-6 IN THE PRESENCE OF Ti(4Al, 4Mn) ALLOY

Test	CO		SiF ₄		CO ₂		BF ₃		COF ₂		CF ₃ COF		C ₂ F ₆		CF ₄		Others	
	mg	% ^a	mg	% ^a	mg	% ^a	mg	% ^a	mg	% ^a	mg	% ^a	mg	% ^a	mg	% ^a	mg	% ^a
36	T ^b	-	817.1	50.5	413.8	25.6	203.9	12.6	86.7	5.4	63.8	3.9	13.0	0.8	19.6	1.2	-	-
37	-	-	69.1	37.7	55.5	30.3	15.8	8.6	19.1	10.4	21.8	11.9	0.7	0.4	1.2	0.7	-	-
39A	-	-	227.1	36.5	182.1	29.2	52.4	8.4	36.8	5.9	25.5	4.1	78.8	12.7	5.2	0.8	14.7 ^c	2.4
39B	-	-	686.8	37.6	589.0	32.3	145.3	8.0	66.1	3.6	44.3	2.4	217.0	11.9	45.4	2.5	30.5 ^c	1.7
39C	-	-	370.5	30.0	370.0	29.9	99.3	8.0	78.1	6.3	50.2	4.1	173.1	14.0	31.3	2.5	64.4 ^c	5.2
42	-	-	0.3	18.8	0.9	56.4	-	-	-	-	-	-	-	-	-	-	-	-
44	1.5	3.1	14.5	30.0	12.8	26.4	0.2	0.4	3.9	8.1	5.6	11.6	5.7	11.8	0.9	1.9	3.3 ^c	6.8
46	0.6	T	830.3	39.0	510.2	24.0	207.5	9.8	98.4	4.6	128.7	6.0	299.5	14.1	36.8	1.7	15.3 ^c	0.7

a) Weight percent of total products. b) Trace. c) These were relatively involatile materials which were collected in the -78°C fraction; these consisted of C₃F₇[OCF(CF₃)CF₂]_xOC₂F₅.

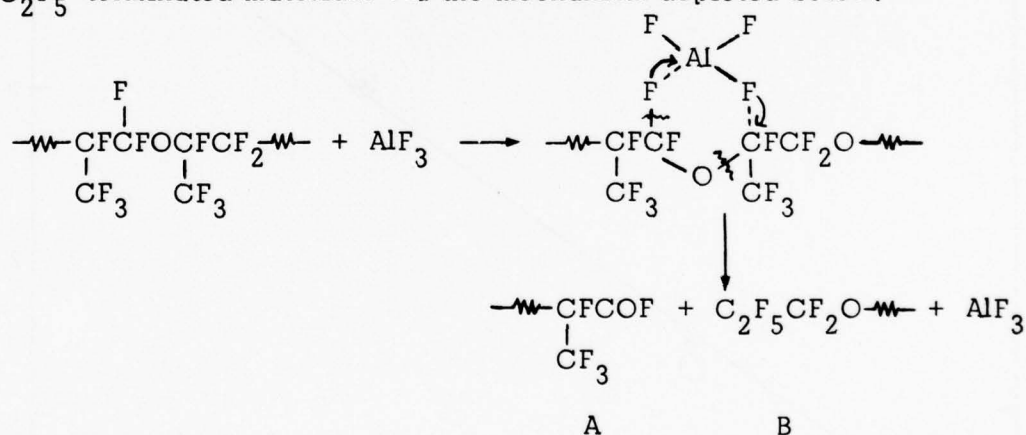
the results of these tests with the corresponding experiments performed in the presence of M-50 coupons, it is apparent that the degradation, as indicated by oxygen consumed and volatiles produced, is significantly accelerated by the presence of the titanium alloy. Actually the 24 hr exposure at 600°F is more severe for the fluid than 48 hr at 650°F in the presence of M-50 (compare Test 36, Table 8 with Test 28A, Table 3). Based on the quantity of volatiles produced and the oxygen consumed at 600°F in the presence of the Ti(4Al, 4Mn) alloy, it can be deduced that at 600°F the degradation involves chain scissions, not just the weak end groups, which is postulated for the M-50 action at 600°F. This stipulation is supported by the observed decrease in molecular weight and viscosity of the residual fluid.

In view of the findings generated in the investigations of the M-50 alloy it was expected (see Table 3, Tests 13 and 21) that possibly at 550°F the titanium alloy merely accelerates the degradation due to the "active" end groups (as was found to take place with M-50 at 600°F). However, this does not appear to be the case with the Ti(4Al, 4Mn) alloy which is evident from Tests 37 and 39A-39C (see Table 8) and even more so from the compilation in Table 10 and the

TABLE 10
RATE OF OXYGEN UPTAKE AND PRODUCT EVOLUTION AS A
FUNCTION OF SUCCESSIVE EXPOSURES OF KRYTOX MLO-71-6
TO OXYGEN AT 550°F IN THE PRESENCE OF Ti(4Al, 4Mn) ALLOY

Test No.	mg O ₂ /g Krytox/hr	mg Prod/g Krytox/hr
37	0.07	0.69
39A-37	0.14	1.32
39B	0.30	3.04
39C	0.46	4.62

graphical presentation in Figure 4. A similar action was observed with M-50 at 650°F (see Figure 2); however, the operative mechanisms must be different. This is shown by the different types of products formed; namely the absence of carbon monoxide and hydrogen terminated fluorocarbons as well as the production of materials of the general formula $C_3F_7[OCF(CF_3)CF_2]_xOC_2F_5$ and C_2F_6 (see Table 9). The reduction in molecular weight of the residual Krytox and the drastic decrease of viscosity in conjunction with the production of the compounds of the type just mentioned would tend to show that chain scissions by a fluorinating agent, e.g. AlF_3 , do take place. This stipulation is in agreement with the work of Gumprecht⁷ who indicated that the attack by AlF_3 leads to chain scissions and formation of C_2F_5 -terminated materials via the mechanism depicted below:



Of the two fragments A can degrade further without assistance from AlF_3 whereas B is a lower molecular weight "Krytox" telomer.

Inasmuch as no degradation was observed in the presence of Ti(4Al, 4Mn) alloy in an inert atmosphere even at 600°F (Test 45, Table 8), it has to be assumed that at that stage AlF_3 is absent and the three metal constituents of the alloy are inactive. On the other hand, it has been shown that even in the absence of metal already at

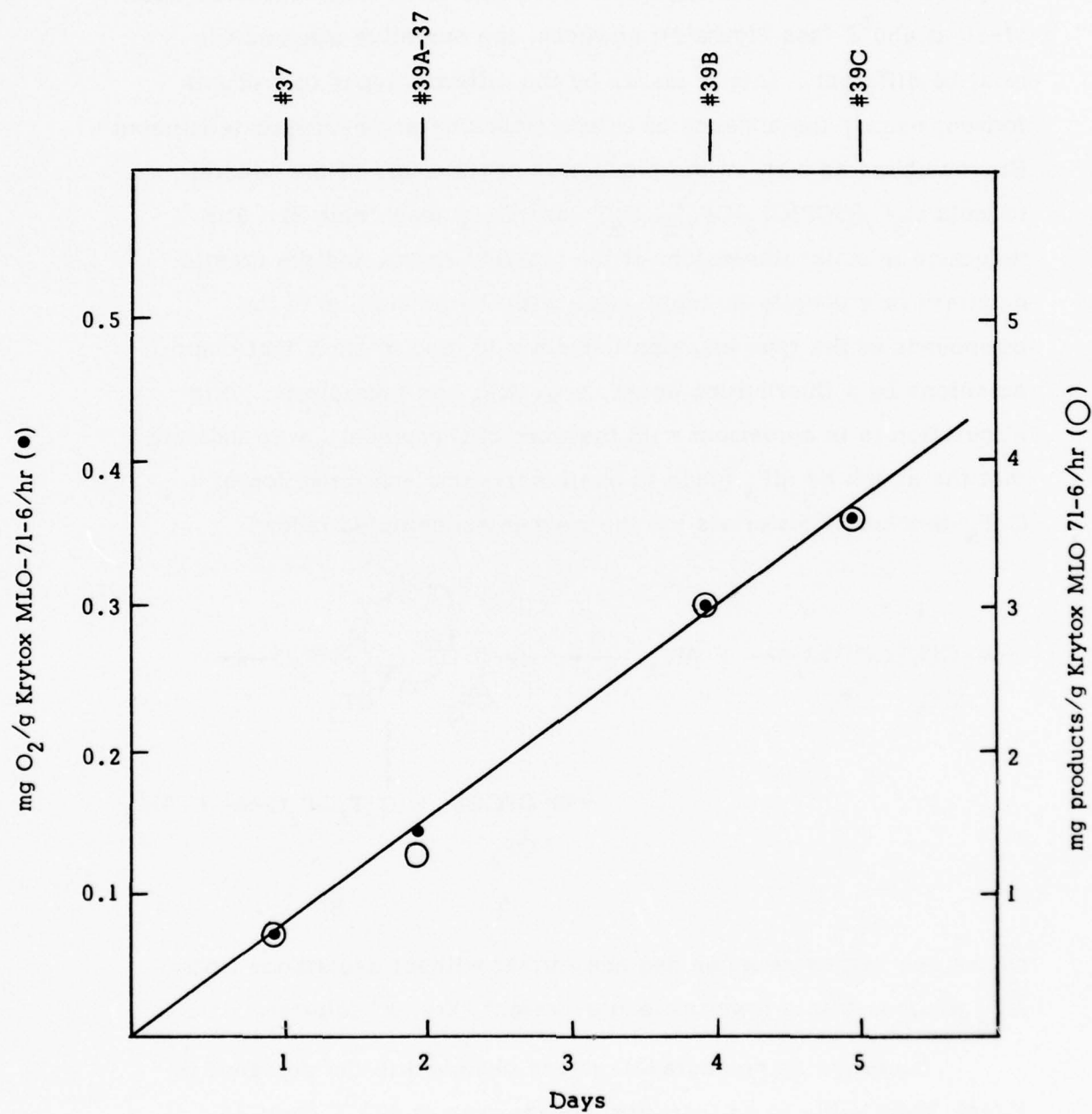


Figure 4. Rate of Oxygen Uptake and Product Evolution as a Function of Successive Exposures of Krytox MLO-71-6 to Oxygen at 550°F in the Presence of Ti(4Al, 4Mn) Coupon

550°F Krytox MLO-71-6 undergoes thermal oxidative degradation (Test 2, Table 1). Consequently, at this temperature AlF_3 is conceivably formed via reaction of e.g. Al_2O_3 (formed by surface oxidation of the alloy) with the fluid's oxidation products, COF_2 and CF_3COF , most likely via the path delineated for SiF_4 production. This type of a process would also explain the rate increase with time (see Figure 4) since the concentration of AlF_3 would increase as degradation would proceed. The postulation regarding AlF_3 formation and its action is strongly supported by Test 43 (Table 8) wherein pretreated Krytox MLO-71-6 (i.e. fluid free of the weak end groups) was employed and where the extent of degradation as measured by volatiles produced and oxygen consumed and as judged by coupon appearance changes was almost nil as compared to Test 37 in which the as received Krytox MLO-71-6 was used. Similar results were obtained in experiment 44, which was conducted in the vicinity of 600°F. Thus it would seem safe to postulate that at least up to 600°F oxides of the metals present in the Ti(4Al, 4Mn) alloy do not degrade hexafluoropropylene oxide derived telomers, providing these are terminated by a perfluoroalkyl moiety, i.e. compositions of the type $\text{C}_3\text{F}_7[\text{OCF}(\text{CF}_3)\text{CF}_2]_x\text{OR}_f$.

The hypothesis has been advanced in the previous discussion that the anti-oxidant/anti-corrosion additive MLO-76-30 functions by preventing the weak end group initiated degradation of Krytox. In agreement with this theory virtually no degradation took place by subjecting 1% of MLO-76-30 in Krytox MLO-71-6 for 24 hr to oxygen at 550°F and 600°F in the presence of a Ti(4Al, 4Mn) coupon (see Tests 40 and 42, Table 8). Comparing experiments 34A and 41 (Table 1), it is apparent that the additive, in the absence of metal, reduced oxygen consumption and volatile products formation by factors of 8

and 90, respectively; however, the really drastic reduction becomes apparent in the presence of the titanium alloy (compare Tests 36 and 42, Table 8) where these factors are 80 and 1400, respectively. The apparently much greater effectiveness of the additive in reducing volatiles production as compared with its effectiveness in reducing oxygen consumption must be attributed to the oxygen-additive interaction as discussed in Section 3 above. The essentially unchanged viscosities and the lack of coupon weight gains or losses further illustrates the additive action. It should be added that the coupon after Test 40 was shiny but of a golden color, whereas after Test 42 it was dull with a reddish tinge; in all the other runs with Ti(4Al, 4Mn) alloy, where extensive fluid degradation occurred, the coupons were invariably coated by a white deposit.

Comparing experiment No. 43, wherein pretreated fluid was utilized, with Run 40, which was conducted under analogous conditions but in the presence of the additive MLO-76-30, it is apparent from the oxygen consumed, volatiles produced and coupon appearance that the results were identical. Thus the pretreatment was as effective as the additive at 550°F in arresting metal corrosion and fluid degradation. At "600°F" (Run 44), however, the additive was more effective by a factor of 20 than the pretreatment as shown by oxygen consumed and volatiles formed. On the other hand, it has to be noted that in Run 44 the temperature was 605°F whereas in Test 42 it was 600°F. It is possible, yet unlikely, that this difference in temperature could be responsible for the results observed inasmuch as at 650°F both the pretreatment and the additive were found to be totally ineffective. It should be noted that the pretreatment reduced the fluid degradation at 605°F (Run 44) as compared to analogous conditions (at 600°F) using the as received

Krytox MLO-71-6 (see Test 36) by a factor of 30 with respect to oxygen consumed and volatiles produced, but the coupon itself was covered by a white film.

In the case of M-50 alloy, it was found that the use of more than one coupon (see Tests 20 and 33; Table 3) failed to significantly increase oxygen consumption and volatiles production. In the case of Ti(4Al, 4Mn) alloy, as can be seen from comparison of Tests 36 and 46, more extensive degradation took place; however, it was less than would be expected from the relative surface area increase.

5. Metal Surface Analyses

Under this program only very preliminary surface analyses were performed and these were limited to the M-50 investigations. The actual analyses were conducted by Seal, Inc., using secondary ion mass spectroscopy (SIMS) and ion scattering spectrometry (ISS). The results of the latter analysis were of an unusual nature and did not lend themselves readily to interpretation; consequently, the major effort was concentrated on SIMS analyses.

To allow meaningful deductions, in addition to metal coupons subjected to specific tests, as identified by the test sample designation corresponding to that given in Table 3, one coupon as received, one polished and washed, and one coupon treated in nitrogen at 650°F for 24 hr in the absence of fluid were also submitted to Seal, Inc. for analysis.

The results of the positive and negative SIMS analyses at $\sim 950\text{\AA}$ below the surface are presented in Tables 11 and 12, respectively. Before discussing these results it should be pointed out that a detailed

TABLE II
COMPLETE POSITIVE SIMS, $^3\text{He}^+$ PROBE GAS: 900-1000 Å BELOW SURFACE

Ion	Sample ^{a)}												Identification
	AR	P	HT	12	13	14	16	17	18	20T	20M	20B	
10			300			40			60	50	40	70	¹⁰ B
11			1180			160			240	140	230	210	¹¹ B
12				310	400	630	1440	17000	820	250	530	540	¹² C
13							80	320	80	40	60		¹³ C, CH
16		60		60	120	50					80	30	O
19			1000	800	1440	1920	1220	1280	3140	1050	1900	1750	F
23	1140	1960	4840	1180	2400	1460	200	800	3980	480	800	5530	Na
24		120	120	200	200	50		280	320		70	100	C ₂ , Mg
27	160	140	380	330	400	200			200	90	160	830	Al
28	170	120	2660	370	340	380	60		300	340	350	310	Si, C ₂ H ₄ , etc.
29			260										
31						70	2700	2080	120		60	100	CF
39	265	840	1200	580	860	430	220	760	1440	210	320	380	³⁹ K
40	90	140	140	230	460	80		120	340	60	130	90	⁴⁰ Ca
41		80	60	70	40	40			140		40	40	⁴¹ K
45			120										?
47			220				480	120					SiF, COF
50			200			500	660	360	300		200	200	CF ₂
51	430	860	1180	1200	1800	1400			1300	600	900	600	⁵¹ V
52	610	1080	2380	4000	6200	6400	360	1840	4900	3000	4100	3400	⁵² Cr
53	115	140	340	600	1000	1100		320	800	500	600	600	⁵³ Cr
54	100	160	920	2500	4600	5200	460	1400	3900	2000	3100	3100	⁵⁴ Fe, ⁵⁴ Cr
56	1150	1820	10660	27500	46200	44600	5700	14800	40200	22800	31900	30700	⁵⁶ Fe
57			340	1000	2000	2100		480	1600	1000	1000	1000	⁵⁷ Fe
69							5820	1320					CF ₃
70					152	124							VF
71				156	220	334		242			270	168	CrF
72				184	352	426				84	210	160	CrF
73				270	550	732				204	350	248	CrF, FeF
75				652	642	1414	1026	1242		464	1142	1108	⁵⁶ FeF
80							136	76					
82							200						⁵⁶ FeO
92		78	72	156	166	198	340	?	70	46	108	86	⁹² Mo
97							280	?					CF ₂ COF
98				130	230	186					162	90	⁹⁸ Mo
100				66	128	68	2120	510	116	32	80	60	C ₂ F ₄
108				66	78	96				36 ?	46 ?	36	
112				262	406	350	66		272	110	216	130	
114	108	76	146	90	78	124				62	72	76	¹¹⁴ Sn
116				42	62	70				30	66	36	¹¹⁶ Sn
119							1264	230					C ₂ F ₅
128			48	72	100	104	118		62			46	C ₂ F ₄ CO ?
131							646	126					C ₃ F ₅
139	484												La
147							248						C ₂ F ₄ COF
150							1202	202					C ₃ F ₆
155	156												LaO
157	66												
169							1350	182					C ₃ F ₇
181							120	48					C ₄ F ₇

a) AR = as received, P = polished, HT = heat treated at 650°C, 24 hr, N_2 , no fluid; T = top, M = middle, B = bottom; all numbers are run numbers.

TABLE 12
COMPLETE NEGATIVE SIMS: ${}^3\text{He}^+$ PROBE GAS: 900-1000 Å BELOW SURFACE

Ion	Sample a)												Identification
	AR	P	HT	12	13	14	16	17	18	20T	20M	20B	
12	350	100											C
13	425	115											¹³ C, CH
16	495	305	420	1800	2200	1020			300	580	420	380	O
17	145			300	480								OH
19	190	205	1530	11620	15800	13620	340	730	12320	9480	9840	9120	F
24	125	120											C ₂
35	240	240	380	180	400	200					220	140	³⁵ Cl
37	125	120	200		240	120					100		³⁷ Cl

a) AR = as received, P = polished, HT = heat treated at 650°F, 24 hr, N_2 , no fluid; T = top, M = middle, B = bottom;
all numbers are run numbers.

analysis of the data collected is not possible due to limitation of funds, absence of reliable ISS results, and the presence of a large variety of species in the surface commonly not encountered in metal surface analysis work. Furthermore, this presence of a large variety of species in the surface makes a comparison of different samples difficult since a large abundance of one species will decrease the extent of ionization of another species. When comparing the output at 56 (^{56}Fe), which may serve as an "internal standard", it can be seen (Table 11) that the counts registered can vary by a factor of 40 (1,150 in the "as received" (AR) sample compared to 46,200 in Test sample 13). However, it can definitely be discerned that the untreated coupons (AR and P in Table 11) have the iron present in considerably lower states of activation than all the other samples. Test sample 16 (5,700 counts at ^{56}Fe) would seem to be an exception; yet when taking under consideration the relatively large abundancies at 31 (CF) and 69 (CF₃) the relatively low 56 output may become understandable.

It is also clear that all samples exposed to the fluid contain fluorine and metal fluorides in the surface (output at 19, 70-75). The presence of a 19 signal in the SIMS of the "heat treated" (HT) coupon (heated at 650^oF for 24 hr in nitrogen in the absence of fluid) seems surprising; however, when considering the presence of ^{10}B , ^{11}B , ^{28}Si , and e.g. SiF (47) in the surface it must be concluded that the walls of the previously used and therefore etched decomposition tube had retained fluorine-containing species despite washing and flaming, which during the 24 hr heating period were released as, e.g., BF₃ and SiF₄; these species apparently became deposited on the coupon surface. These results of the positive SIMS are supported by the negative SIMS spectra (see Table 12).

A further definite conclusion from the positive SIMS data is that those metals present in the M-50 steel, which can form volatile fluorides, are severely depleted with respect to iron in the surface at least to a depth of $\sim 1,000 \text{ \AA}$. This becomes particularly evident when all outputs are normalized for a constant ^{56}Fe count of 1,000. Inspection of Table 13 shows that vanadium and chromium in all coupons exposed to Krytox MLO-71-6 are reduced to 10-20% of the value found in the untreated samples. Even the "heat treated" coupon (HT) showed this depletion, although to a lesser degree. It is of interest that the degree of "volatilization" of vanadium and chromium out of the surface apparently is the same irrespective of temperature (see Test samples 12 and 14, Table 13; 550 and 650 $^{\circ}\text{F}$, respectively), exposure time (see Test samples 14 and 17; 24 and 216 hr, respectively), or atmosphere (see Test samples 17 and 18; oxygen and nitrogen, respectively).

An analysis of concentration variations with depth into the surface is rather inconclusive. One would expect the concentration of those species deposited or formed (e.g., fluorides and fluorocarbon fragments) to be highest at a shallow depth and to decrease with increasing distance from the surface. The opposite would be expected for the constituents of M-50, e.g., iron, chromium and vanadium. Examining Table 14 it can be seen that this trend is followed in all significant masses by Test sample 17. The fluorocarbon fragments 19 (F), 31 (CF), 50 (C_2F_4), and 69 (CF_3) and the fluorides, e.g., 75 (FeF) are less abundant at greater depth than in the surface, whereas the abundancies for the metals 52 (Cr) and 56 (Fe) increase with greater depth. However, in Test sample 14 this trend for the metals (51, 52, 56) is reversed for unknown reasons, as it is reversed for the fluorine-containing species (19 and 31) in Test sample 18. Quite obscure is the finding for Test sample 16 that the concentration of 19 (F) on the surface

TABLE 13
METAL CONCENTRATIONS AT 1.000 Å NORMALIZED TO ^{56}Fe

Ion	Sample a)											
	AR	P	HT	12	13	14	16	17	18	20T	20M	20B
⁵¹ V	373.9	472.5	110.7	43.6	39.0	31.4	-	-	32.3	26.3	28.2	19.5
⁵² Cr	530.4	593.4	223.3	145.5	134.2	143.5	63.2	124.3	121.9	131.6	128.5	110.7
⁵³ Cr ^{b)}	100.0	76.9	31.9	21.8	21.6	24.7	-	21.6	19.9	21.9	18.8	19.5
⁵⁴ (Cr & Fe) ^{b)c)}	87.0	87.1	86.3	90.6	99.6	116.6	80.7	94.6	97.0	87.7	97.2	101.0
⁵⁶ Fe	1,000.0	1,000.0	1,000.0	1,000.0	1,000.0	1,000.0	1,000.0	1,000.0	1,000.0	1,000.0	1,000.0	1,000.0

a) AR = as received, P = polished, HT = heat treated at 650°F, 24 hr, N_2 , no fluid; T = top; M = middle; B = bottom;
all numbers are test numbers.

b) Natural abundance: $^{53}\text{Cr} = 11.48\%$ of ^{52}Cr ; $^{54}\text{Cr} = 2.74\%$ of ^{52}Cr .

c) Natural abundance: $^{54}\text{Fe} = 6.32\%$ of ^{56}Fe .

TABLE 14
SELECTED INTENSITY VARIATIONS WITH DEPTH; POSITIVE SIMS

Ion	Sample 17			Sample 16			14		18	
	900-1000A	34-40A	° 4A	900-1000A	° 4A	° 4A	900-1000A	° 4A	900-1000A	° 4A
10										
12	17000	23120	28240	1440	2080	2080	630	1620	60	1320
13	320	800	880	80	120	120		110	820	120
19	1280	1400	1520	1220	1000	1000	1920	2250	80	920
23	8 0	4080	6040	200	200	200	1460	4010	3140	3700
28			320	60	120	120	380	330	3980	
31	2080	3840	9200	2700	4600	4600	70	210	2080	120
39	760	1240	2640	220	40	40	430	710	760	1700
41			120					50		100
43			120		60	60				
47	120	280	1120	480	760	760				
50	360	600	1640	660	1200	1200	500	900	300	
51							1400	2200	1300	
52	1840	440	200	360	40	40	6400	12700	4900	300
54	1400	680	400	460	140	140	5200	10000	3900	1380
56	14800	7760	5040	5700	1640	1640	44600	50800	40200	14180
62			160		180	180				
69	1320	3360	13520	5820	10860	10860				
75	1242	1398		1026	1414	1414			510	
92					148	148				
93		142								
97		136		280						
100	510	862	2120		68	68				
119	230	400	1264						62	
128			118		104	104				
131	126	180	646							
147		148	248							
150	202	368	1202							
169	182	426	1350							
181	48	60	120							

(4Å) is slightly lower than at $\sim 1,000$ Å, whereas the concentration variation for fluorocarbon species (31, 50, 69) with distance from the surface is as expected.

To summarize, the SIMS spectra allow the following stipulations to be made: (a) the metals in the coupons exposed to Krytox MLO-71-6 fluid are present in a higher state of activation as compared to the untreated specimens; (b) at ~ 950 Å deep into the surface fluorine, metal fluorides, and species containing C-F and C-F-O entities are present; (c) vanadium and chromium are severely depleted with respect to iron in all the treated samples. The extent of depletion seems to be unaffected by variation of exposure time, temperature, or atmosphere. A comparison of the SIMS spectra obtained at different distances from the surface (4, 40, 900 Å) unfortunately was inconclusive.

SECTION III

APPARATUS AND EXPERIMENTAL PROCEDURES

The sample decomposition tubes and the metal specimen holders were constructed essentially in the same manner as those used in the AFML Micro-O-C test^{2,3} (see Figures 5 and 6) with the exception that the tubes were closed via a 29/42 ground joint adapter with 0-3 mm Teflon stopcock and 10/30 ground joint for ready attaching of the system to the high vacuum line. To provide a greater supply of oxygen for any oxidation process, these adapters were furthermore equipped with a ~250 ml reservoir as shown in Figure 5. For reproducible centering of the metal specimen holder a positioner was constructed which holds the rod of the specimen holder in the center of the 29/42 ground joint as shown in Figure 6.

To reduce the liquid volume the metal coupons' size was scaled down from 3/4" OD, 1/4" ID to 3/8" OD, 1/8" ID. This allowed the use of as little as 6-8 cc of fluid per actual run. For heating of sample tubes in a vertical position, which is necessary in all experiments involving metal specimens, a Lindberg Hevy-Duty box furnace, Type 51232, was modified as follows. A stainless steel sample block (85 x 125 mm, 100 mm high) was equipped with a 9 mm diameter, 83 mm deep center hole to accommodate a thermometer or thermocouple and two 27 mm diameter, 83 mm deep holes, 30 mm center to center along the 125 mm length of the block, to allow the insertion of two sample decomposition tubes. This sample block was placed into the cavity of the box furnace in such a fashion that the bottom of the sample tube was located 170 mm above the bottom of the box furnace (see Figure 7). The box cavity was closed by a 65 mm thick cover made of castable Insulation 22 manufactured by A. P. Green Refractories Co. This cover contains two 27 mm diameter and one 9 mm diameter holes so that two sample decomposition tubes

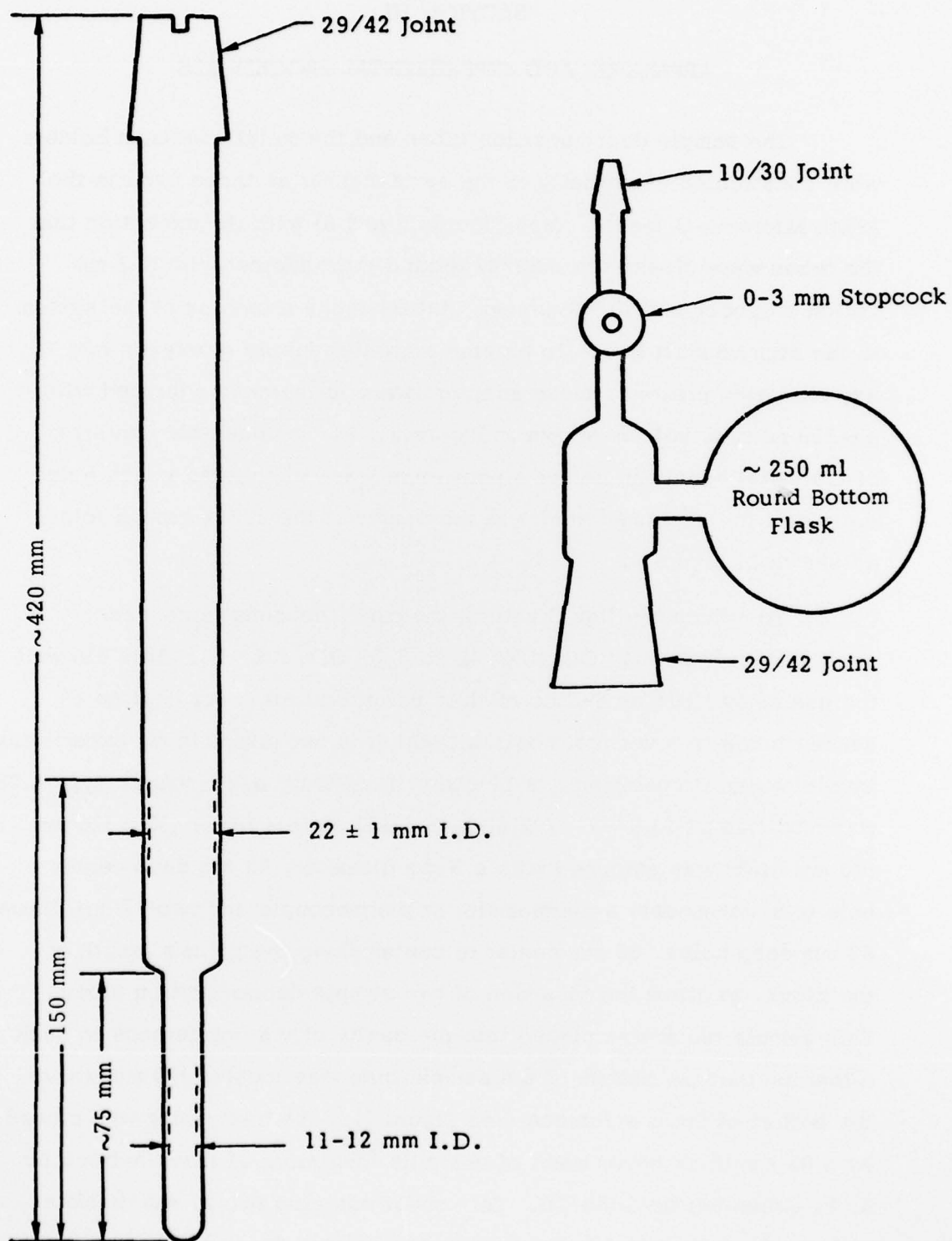


Figure 5. Decomposition Tube and Adapter

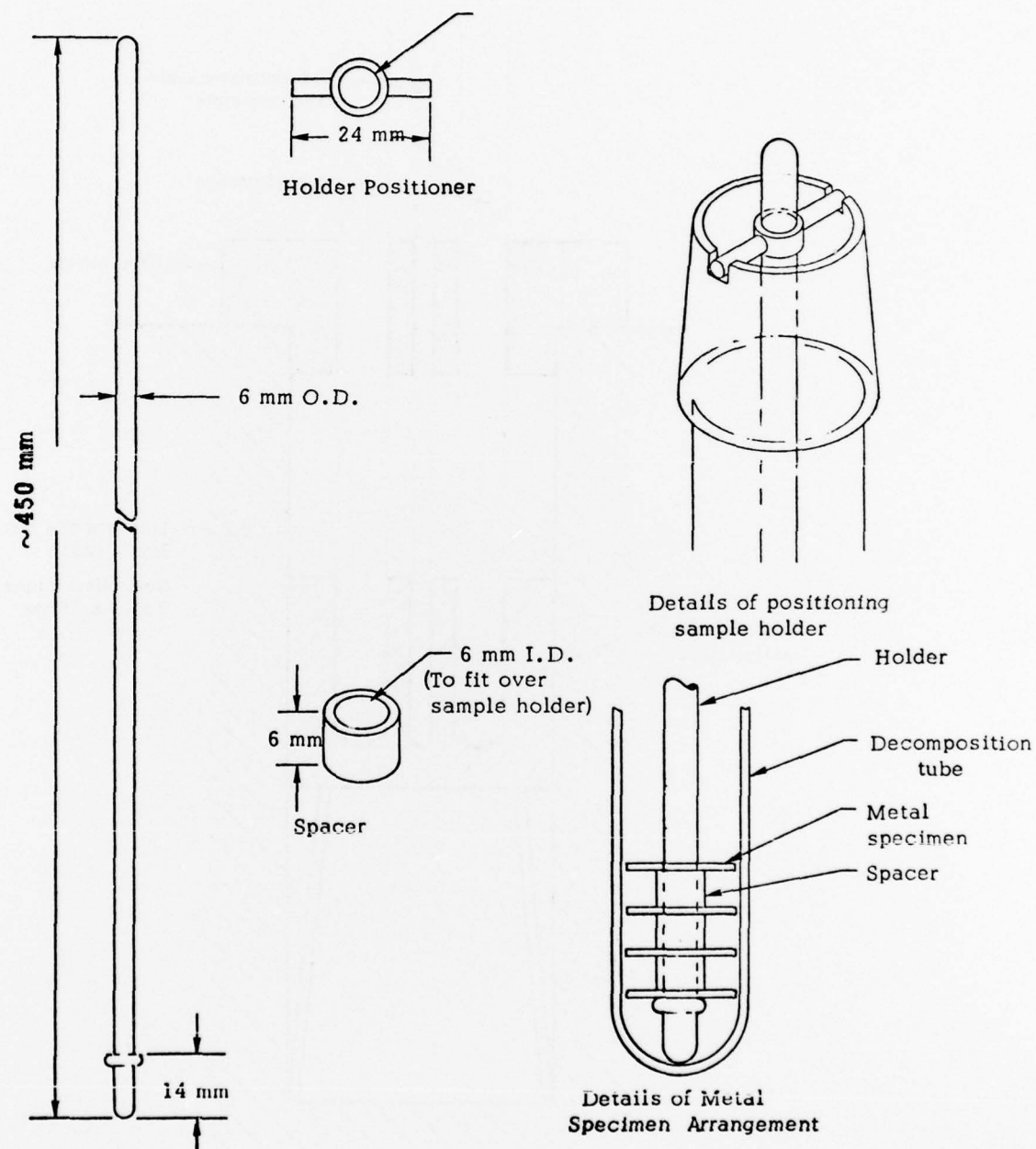


Figure 6. Metal Specimen Holder Arrangement

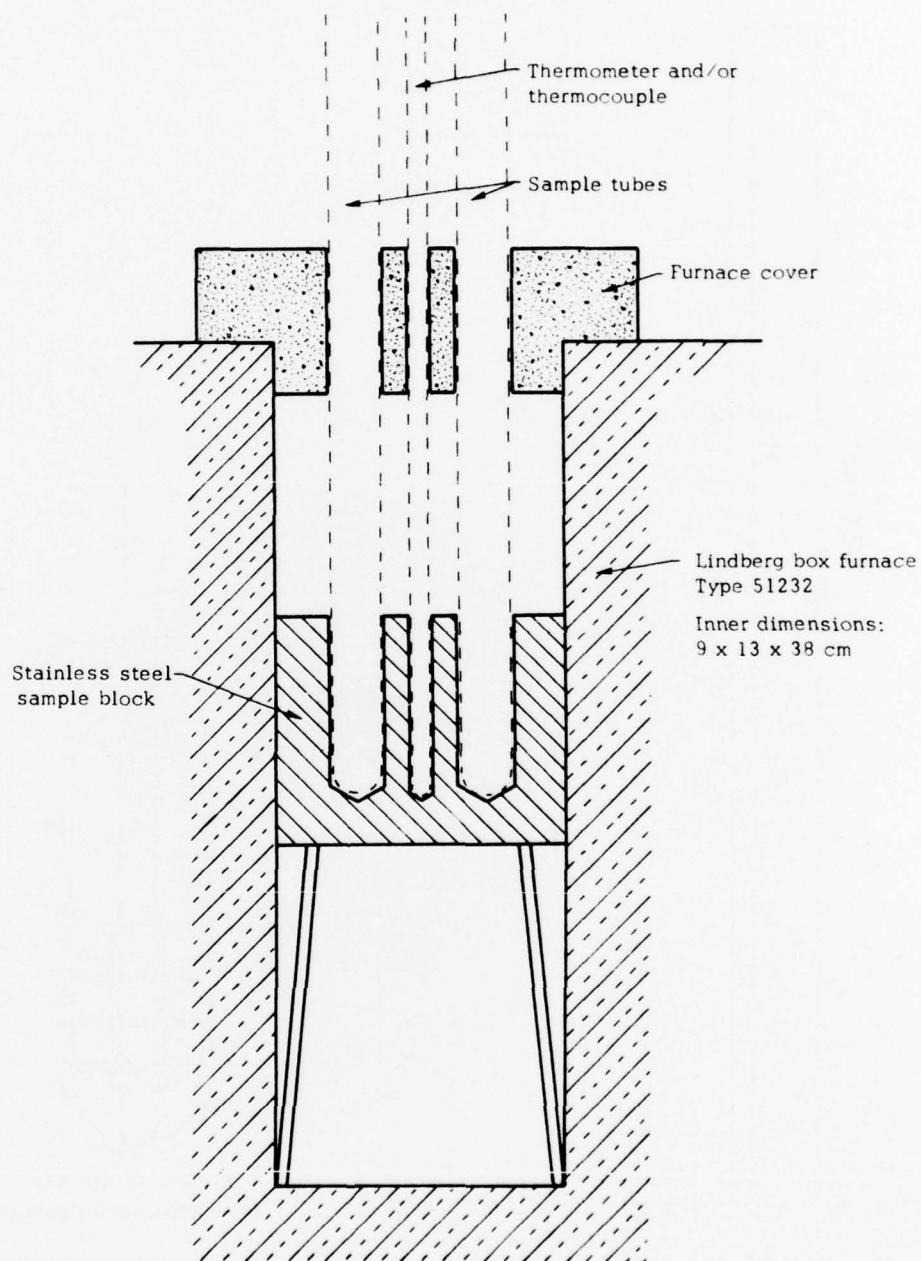


Figure 7. Box Furnace Arrangement

and a thermometer or thermocouple can extend out of the box furnace cavity.

In a typical experiment the fluid was introduced into the degradation tube (see Figure 5) which was then evacuated and filled to a known pressure at a known temperature with a selected gas (air, N_2 or O_2). Inasmuch as the apparatus was calibrated the quantity of gas thus introduced was exactly known. The degradation tube was then inserted into the preheated box furnace and kept there for a specified period of time; throughout this exposure the temperature was continuously recorded. After removal from the furnace the tube was allowed to cool to room temperature, attached to the high vacuum line, and opened. The liquid nitrogen noncondensibles were collected quantitatively, measured, and analyzed by mass spectrometry. The liquid nitrogen condensibles, which were volatile at room temperature, were measured, weighed and analyzed by infrared spectroscopy, mass spectrometry, and GC-MS. The fluid residue itself was weighed and subjected to infrared spectral analysis, differential scanning calorimetry (DSC), molecular weight measurement, and viscosity determinations.

The molecular weight of Krytox was found to be 5500 using a Hewlett-Packard osmometer Model 302. The primary standard used was tris-perfluoro-n-heptyl-s-triazine; measurements were conducted in hexafluorobenzene. In all the determinations of the treated Krytox the original Krytox sample (as received from the Air Force Materials Laboratory) was used as the standard. Consequently, regardless of the absolute value of Krytox molecular weight the relative differences are with respect to this untreated material.

The metal coupons prior to testing were polished using first Norton No-Fil Durite finishing paper Type 4 220A. This was followed

by open coat Silicon Carbide papers grades 400A and 500A, respectively. Subsequently the coupons were washed with Freon 113, dried, weighed, and suspended in the test apparatus (see Figure 6). After the completion of a given experiment, the metal coupons were weighed, after washing with Freon 113 and drying inside an inert atmosphere chamber, visually inspected, and selected specimens were subjected to SIMS (secondary ion mass spectrometry) and ISS (ion scattering spectrometry) analyses.

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